

AD-787 283

DECOMPOSITION OF NITROCELLULOSE USING  
AQUEOUS AMMONIA

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Army Natick Laboratories  
Natick, Massachusetts

July 1974

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER <b>AD-787283</b>
4. TITLE (and Subtitle) Decomposition of Nitrocellulose Using Aqueous Ammonia		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report, March - October 1973
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Libera M. Dogliotti, Wald C. Chalk, Leo A. Spano, Dale H. Sieling		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Pollution Abatement Division, STSNL-YP Food Sciences Laboratory, US Army Natick Lab Natick, Mass. 01760		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 672713-1T762713A031-10 003-BG
11. CONTROLLING OFFICE NAME AND ADDRESS Food Sciences Laboratory U. S. Army Natick Laboratories Natick, Mass. 01760		12. REPORT DATE July 1974
		13. NUMBER OF PAGES 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)  Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Distribution of this report is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Nitrocellulose, Decomposition of and Quantitative Analysis of		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Optimization of reaction conditions necessary for complete decomposition of nitrocellulose using the weak base, ammonium hydroxide, has been accomplished. An infrared spectroscopic procedure was adapted to quantitatively analyze for nitrocellulose down to the low p. p. m. level.		

Technical Report

DECOMPOSITION OF NITROCELLULOSE  
USING AQUEOUS AMMONIA

by

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Project Reference:  
1T762713A031

Series FSL

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Food Sciences Laboratory  
U. S. Army Natick Laboratories  
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in

## FOREWORD

This study was performed under the Pollution Abatement Program of the Pioneering Research Laboratory, Task 10, Project 1T762713A031. The report covers work conducted primarily during the period March, 1973, to October, 1973. The desirability of decomposing nitrocellulose using ammonium hydroxide was suggested by Dr. Dale H. Sieling to Mr. Leo A. Spano. The authors gratefully acknowledge contributions from other personnel of U. S. Army Natick Laboratories, Dr. Edward Ross, Staff Mathematician, for help in the design of the Latin Square Plan experiments, Dr. Derek H. Ball, Head, Organic Chemistry Group, for helpful discussions and background information, and Samuel Cohen, Biologist, for the photomicrographs using the optical microscope and electron microscope.

## TABLE OF CONTENTS

LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	vi
INTRODUCTION	1
OBJECTIVE	3
DISCUSSION	3
EXPERIMENTAL	13
General	13
Solubility of Nitrocellulose in Water	14
Quantitative Analysis for Nitrocellulose	
Using Infrared Spectroscopy	14
Use of Sodium Hydroxide to Decompose	
Nitrocellulose	14
Preliminary Attempts to Decompose	
Nitrocellulose Using Ammonium Hydroxide	15
General Procedure for Degradation of	
Nitrocellulose Using Ammonium Hydroxide	16
Effect of Time on Decomposition of	
Nitrocellulose	16
Latin Square Design for Experiments	17
Determination of Excess Ammonia After	
Decomposition of Nitrocellulose	17
A More Efficient Use of Ammonium	
Hydroxide per Gram of Nitrocellulose	
to Effect Complete Decomposition	17
CONCLUSIONS	19
BIBLIOGRAPHY	21

## LIST OF TABLES

1. Latin Square Plan and Suggested Experiments	12
2. Additional Experiments	12
3. Results of Latin Square Plan Experiments and Additional Experiments	18

### LIST OF FIGURES

1. Photomicrographs of cellulose, nitrocellulose, and ammonium hydroxide treated nitrocellulose. 5
2. Photomicrographs of cellulose, nitrocellulose and ammonium hydroxide treated nitrocellulose as observed through the electron microscope. 6
3. Straight line calibration curves relating absorbance at  $825\text{ cm}^{-1}$  to percentage concentration of nitrocellulose in acetone. (A, B, C are different concentration ranges.) 9

## ABSTRACT

Optimization of reaction conditions necessary for complete decomposition of nitrocellulose using the weak base, ammonium hydroxide, has been accomplished. An infrared spectroscopic procedure was adapted to quantitatively analyze for nitrocellulose down to the low p. p. m. level.



## INTRODUCTION

Waste waters resulting from the manufacture of munitions constitute a major pollution problem. Nitrocellulose "fines" are present in waste waters resulting from its production and methods are needed to collect and either recycle or destroy these waste products. Centrifuges are to be used to concentrate the fines; however, there are times when large amounts of nitrocellulose of uncertain purity cannot be recycled and must be destroyed.

Some of the simpler methods used to destroy nitrocellulose are:

1. Burning.
2. Reaction with water at elevated temperatures and pressures.
3. Reaction with acid.
4. Reaction with base.

1. Burning in open pits is done industrially. However, it is frowned upon because of the huge evolution of  $\text{NO}_x$  which is released to the environment. If burning is carried out in a confined space, appreciable amounts of HCN are developed. <sup>(1)</sup>

2. If nitrocellulose is treated with water at  $190^\circ\text{C}$  and at elevated pressures in a sealed unit, the gases evolved were shown to consist of  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$  and  $\text{N}_2$ . In the aqueous phase, HCN,  $\text{NH}_3$ , formic, tartaric, hydroxypyruvic, nitric and nitrous acids were detected. <sup>(2)</sup>

3. Reaction of nitrocellulose with acid is much slower than reaction with alkali<sup>(3)</sup>. In concentrated sulfuric acid, nitrocellulose decomposes slowly, losing nitric acid to form a sulfuric ester<sup>(4)</sup>. Dilute nitric acid over a long period of time causes a partial denitration and formation of oxycellulose.<sup>(4)</sup>

4. There are many references<sup>(5 - 10)</sup> available reporting on the use of strong alkali such as sodium hydroxide for decomposing nitrocellulose. The use of aqueous alkalies to saponify nitrocellulose does not yield cellulose and the corresponding alkali nitrate but gives mainly the alkali nitrite and a large number of decomposition products of cellulose including CO, CO<sub>2</sub>, oxalic, malic, glycolic, trihydroxyglutaric, dihydroxybutyric, malonic, tartronic and hydroxypyruvic acids. The most extensive quantitative investigation of the alkaline decomposition of nitrocellulose has been carried out by Kenyon and Gray.<sup>(11)</sup>

Very few references report the use of a weak base such as ammonia in water for decomposing nitrocellulose. In fact, Patent No. US 2,404,887 suggests the use of an aqueous solution of ammonia at room temperature for one hour for stabilizing nitrocellulose. The two literature references which report on the action of ammonia in water on nitrocellulose are concerned with the reduction in viscosity of such solutions. Danilov and Mirlas<sup>(12)</sup> report that the denitration is accompanied by oxidation of the nitrocellulose with the coincidental reduction of  $\text{NC}_3^-$  to  $\text{NO}_2^-$ . The loosening of the micelle structure of that part of nitrocellulose which is chemically unchanged causes a reduction in viscosity. Chernitskaya, Kargin and Gutenmakher<sup>(13)</sup>

report that ammonia reacts with nitrocellulose requiring a temperature of 60-65°C resulting in the decomposition of nitrocellulose which, in turn, causes a lowering of the viscosity. A Canadian patent, No. 313,339, suggests that nitrocellulose can be saponified by treatment with an atmosphere resulting from the vaporization of a 28% aqueous ammonia solution at a temperature not above 30°C.

### OBJECTIVE

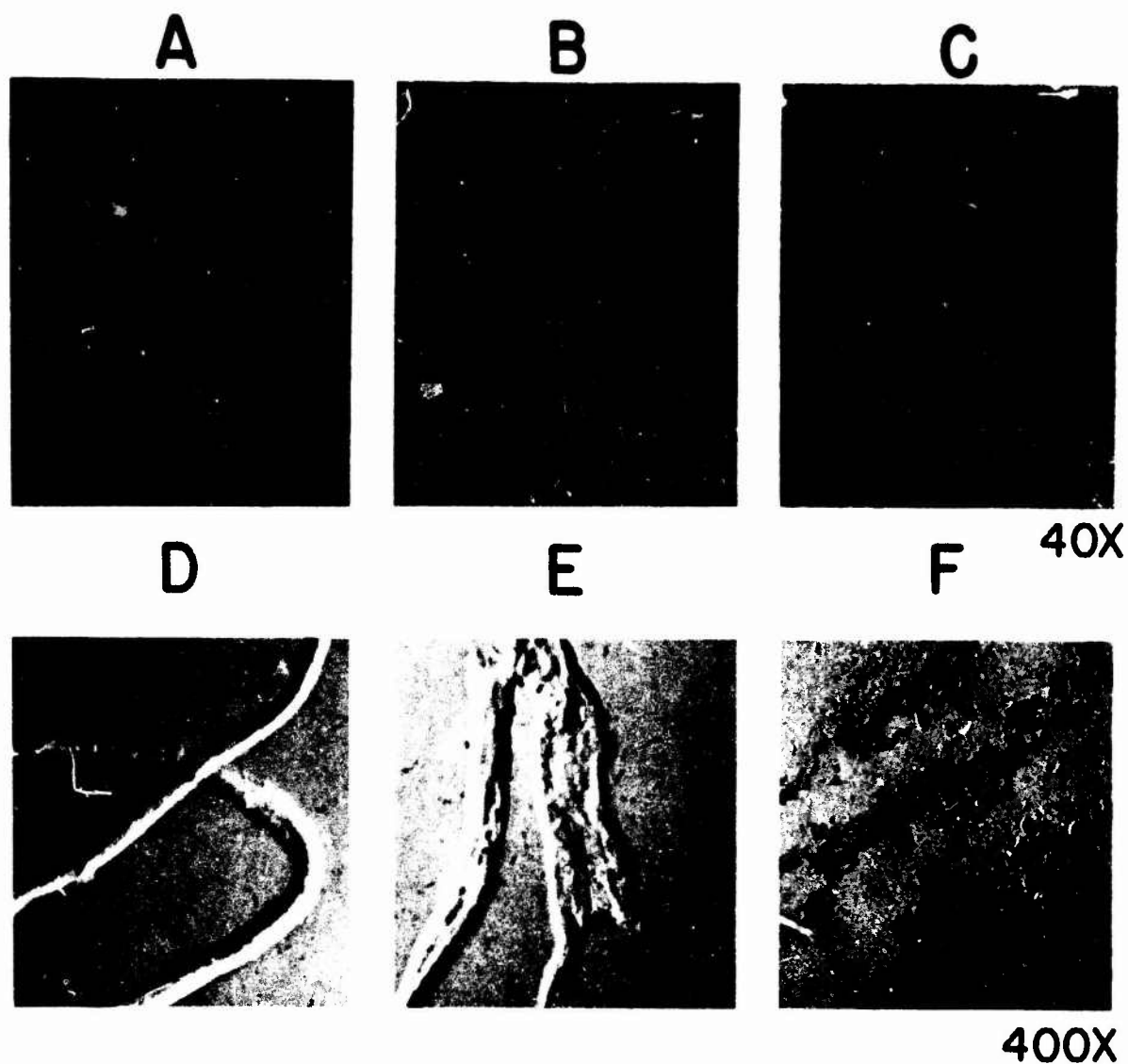
The objective of this research was to design an economical and non-polluting method of decomposing nitrocellulose. The most efficient method for breakdown of nitrocellulose involves the use of a strong base such as sodium hydroxide. However, in addition to economical considerations, addition of large amounts of sodium ions to the environment is unwise. Therefore, it was decided to study the effect of the weak base, ammonium hydroxide, on nitrocellulose. The preferred use of ammonium hydroxide as reactant provides an additional advantage in that the bulk of the nitrate ester groups give ammonium nitrite and nitrate and these products could become important in a landfill site as a source of fertilizer. Since quantitative analysis of nitrocellulose forms an important part of this project, a reliable method of analysis had to be devised.

### DISCUSSION

In waste waters, nitrocellulose exists in the form of "fines" of particle size 0.5 - 1.0 $\mu$  in diameter and 10-40 $\mu$  in length. The Handbook of Chemistry and Physics states that nitrocellulose is insoluble in water; however, in order to analyze properly for nitrocellulose as a pollutant in waste waters or as residual starting

material in a decomposition reaction, it was necessary to ascertain limits of solubility. Experimentation showed that the solubility of nitrocellulose in water at room temperature was in the range 0-3 mg./liter. Heating the sample at 85°C for 10 hr. gave the same results. A range is quoted because of hygroscopicity problems encountered during the weighing of the dried nitrocellulose samples.

During the procedure in which nitrocellulose is decomposed using ammonium hydroxide, several quick diagnostic non-quantitative tests as well as an analytical method for the determination of residual nitrocellulose were used. Microscopical examination of samples using both ordinary and polarized light gave a good indication as to the presence or absence of nitrocellulose. Ambronn<sup>(14)</sup> mentions the value of the polarization microscope in determining degree of nitration. Figure 1 shows photomicrographs of cellulose, nitrocellulose and nitrocellulose after ammonium hydroxide treatment. These are mounted in glycerine and taken with an optical microscope at 40X and 400X magnification using white light. There is no evidence of crystallinity in the photomicrograph of the treated nitrocellulose and a breakdown of filament wall structure is observed. Figure 2 shows photomicrographs of the above specimens after gold-palladium coating as observed through the scanning electron microscope (2000X). It is interesting to note that due to the nitration of cellulose, the nitrocellulose filament increases in size causing rupturing of the wall in addition to fibrillation. At this magnification, photograph F shows complete physical breakdown of the nitrocellulose structure after treatment with ammonium hydroxide.



**Figure 1. Photomicrographs using optical microscope and white light. (A) and (D) cellulose; (B) and (E) nitrocellulose; (C) and (F) solids after ammonium hydroxide heat treatment.**

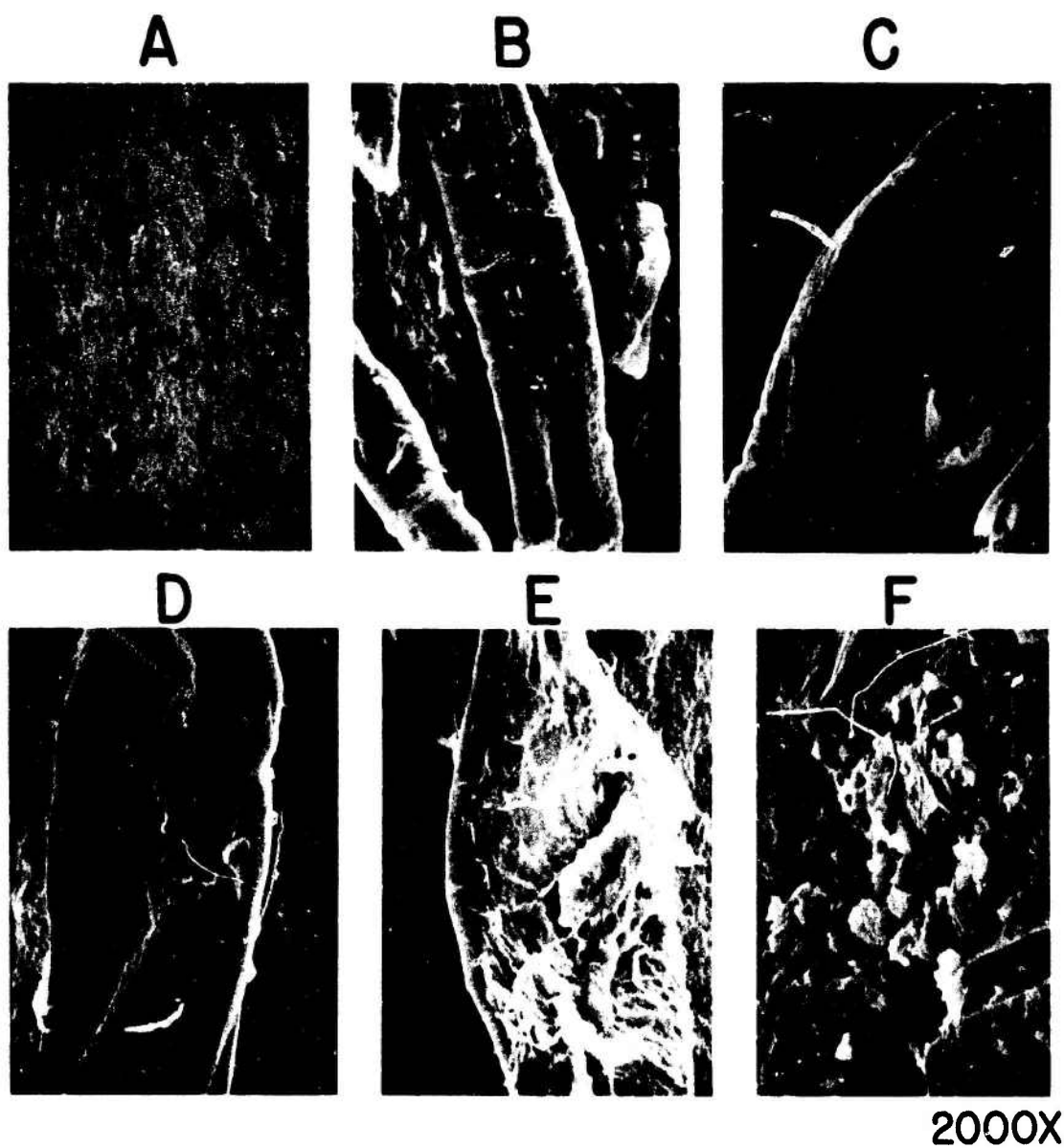


Figure 2. Photomicrographs using electron microscope. (A) gold-palladium surface; (B) and (C) cellulose; (D) and (E) nitrocellulose; (F) solids after ammonium hydroxide heat treatment.

The Molisch test for carbohydrates<sup>(15)</sup> was applied to samples of the residual solids as well as the concentrated filtrate resulting from the treatment of nitrocellulose with ammonium hydroxide. Standard dispersions of cellulose and nitrocellulose gave positive Molisch tests. The residual solids from the filtration were intensely black and masked the color test so that no conclusions could be reached; when diluted samples were used, a negative test for carbohydrate was observed. The concentrated filtrates which contained the bulk of the decomposed nitrocellulose gave negative tests for carbohydrate. Decomposition of nitrocellulose can occur in three ways, saponification of the nitrate group to give cellulosic material, rupture of glycosidic bonds to give smaller molecular weight chains and, finally, intermolecular oxidation of the anhydro glucose units themselves. The negative Molisch test indicates that the decomposition has progressed to the point that even the glucose units have been broken down. Paper chromatographic analysis showed no evidence of glucose or glucose oligosaccharides. However, streaking caused by the presence of inorganic compounds precluded any definitive information.

Infrared spectroscopy was used both for the qualitative and quantitative analysis of nitrocellulose. A good indication for the presence or absence of nitrocellulose involves examination of the infrared spectrum at the three strong bands occurring at 825, 1275 and  $1650\text{ cm}^{-1}$ . These are characteristic of the nitrate group. The infrared spectroscopic procedure used for quantitative aspects of the problem was based on one reported by Rosenberger and Shoemaker<sup>(16)</sup>.

The procedure is relatively simple, the absorbance is measured at  $825\text{ cm}^{-1}$  using the zero base line technique with acetone as blank. The nitrocellulose content is determined from a calibration curve prepared using standard nitrocellulose solutions (see Figure 3). The range quoted in A of Figure 3 is used when the nitrocellulose content is known to be very small. The specific wave length used ( $825\text{ cm}^{-1}$ ) is not subject to interferences from other cellulosic materials. However, if inorganic nitrate interferes, another procedure is used so that the  $1650\text{ cm}^{-1}$  absorption band is utilized with tetrahydrofuran as solvent<sup>(17)</sup>. A calibration curve using these changes was also prepared. Both procedures are capable of measuring nitrocellulose down to the 1-5 p. p. m. range.

Since sodium hydroxide is commonly used to decompose nitrocellulose<sup>10, 11, 18, 19</sup>, a series of experiments were carried out using this reagent in order to determine conditions which would result in complete decomposition of nitrocellulose. A secondary goal was to determine the applicability of the quantitative infrared spectroscopic analysis procedure to the degradation method. Heating a 5% dispersion of nitrocellulose in 2% aqueous sodium hydroxide at  $95^{\circ}\text{C}$  for 30 minutes resulted in 31% residual unreacted nitrocellulose. When the sodium hydroxide concentration was increased to 3% and the other reaction conditions kept the same, only 5% unreacted nitrocellulose remained. By increasing the temperature from  $95^{\circ}$  to  $98^{\circ}\text{C}$ , the nitrocellulose content was further reduced to 3%. Complete reaction (0% nitrocellulose) was achieved using 3% aqueous sodium hydroxide at  $98^{\circ}\text{C}$  for 1 hr. A check was made to ensure that no nitrocellulose was lost in filtration. The filtrate was concentrated and examined using the infrared procedure and found to contain no nitrocellulose.



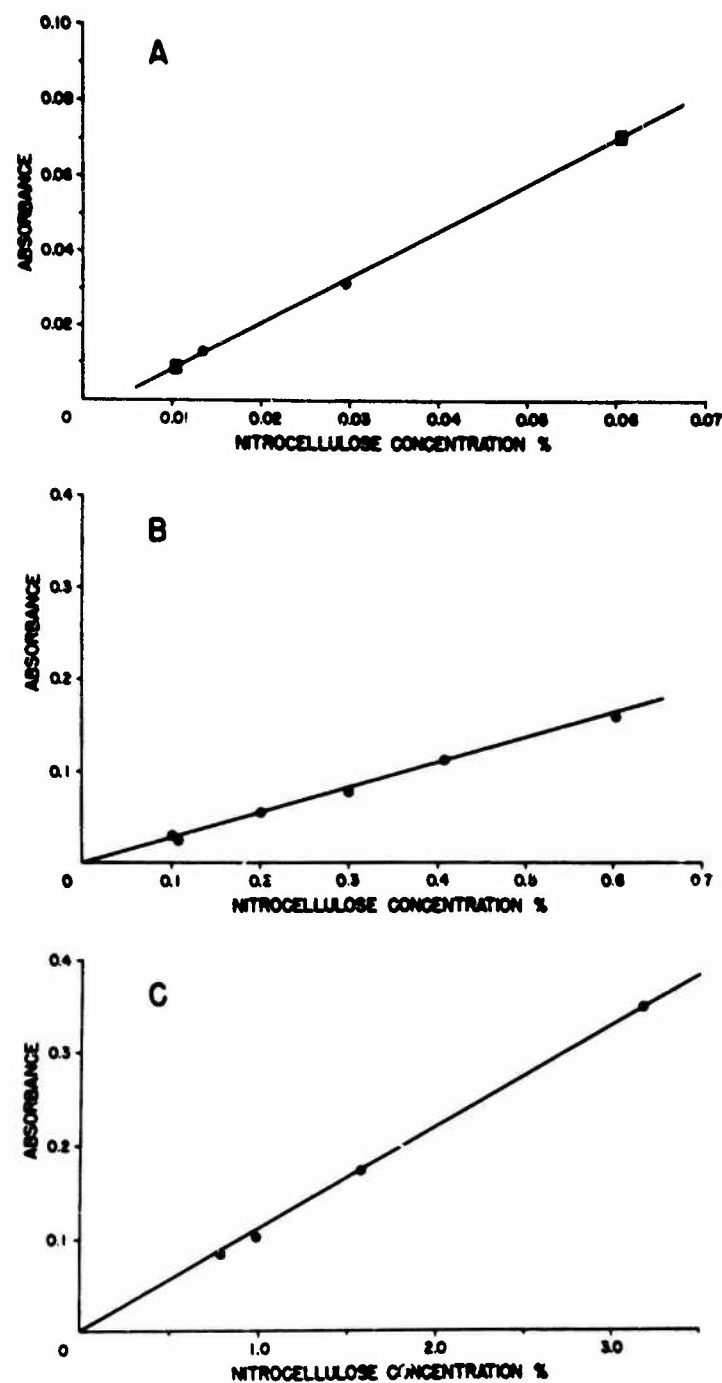


Figure 3. Variation of absorbance with concentration of nitrocellulose at  $825\text{ cm}^{-1}$  using acetone as the solvent. (A) 0.50 mm cells; (B) 0.103 mm cells; (C) 0.041 mm cells.

As mentioned previously, many literature references<sup>(10, 11, 18, 19)</sup> discuss the use of a strong base such as sodium hydroxide to decompose nitrocellulose; however, very little has been reported on the use of a weak base such as ammonia in water for such a purpose. The first preliminary attempts using ammonium hydroxide were done in order to determine whether or not the weak base could effectively destroy the nitrocellulose. Room temperature experiments for long periods of time (5 days) resulted in a 40% yield of a water-insoluble residue. However, analysis showed that only 3% of unreacted nitrocellulose remained. It appears that most of the insoluble residue consists of cellulose-like products, i.e. the room temperature base decomposition was strong enough to saponify the nitrate ester groups but not strong enough to completely break down the polymeric chain. In an experiment using conditions similar to those used for complete sodium hydroxide decomposition of nitrocellulose, a 10% solution of ammonia in water was only able to destroy approximately 50% of the starting material.

A general procedure was adopted in which the objective was manipulation of reaction conditions in order to achieve complete decomposition of the nitrocellulose. An elevated temperature,  $73 \pm 1^{\circ}\text{C}$  was chosen because preliminary experiments indicated that a temperature in that order was necessary to effect complete reaction within a 24 hr. time period. The literature<sup>(13)</sup> also recommended reaction temperatures of at least  $50-65^{\circ}\text{C}$ . The reflux condenser was necessary to ensure that all the ammonia was available to be used in the reaction and not allowed to escape from the reaction vessel.

Periodic checks using moistened pH paper at the reflux condenser outlet showed no indication of escaping ammonia.

A series of experiments were completed to determine the shortest length of time needed to decompose a 5% suspension of nitrocellulose using a large excess of ammonia (10%). The data indicated the presence of (not determined quantitatively) nitrocellulose after 4 hr. reaction time but none after 8 hr. It is interesting to note that after zero nitrocellulose content is reached (8 hr.) the amount of water insoluble residual solids continues to decrease as longer reaction times (16 and 23 hr.) are used.

From the preliminary experiments it was decided to choose reaction time variations of 4, 7 and 12 hrs., ammonium hydroxide concentration variations of 5, 10 and 15% and nitrocellulose concentration variations of 5, 10 and 15%. In order to arrive at a set of optimum reaction conditions from the above selections, 27 experiments would be required. The use of a Latin Square approach decreases the number of needed experiments to nine and the most influential reaction condition is determined. Construction of the Latin Square plan and suggested experiments are shown in Table 1. The results of the experiments are shown in Table 3. Experiments 1, 8 and 9 were carried out according to the Latin Square Plan and resulted in incomplete decomposition of the nitrocellulose. Experiments 4 and 7 gave complete decomposition of the nitrocellulose using a large excess of ammonia. Experiment number 5 effected complete decomposition using less ammonia per gm. of nitrocellulose. Specifically, a 10% dispersion of nitrocellulose was decomposed by a 10% solution of ammonia in water in 12 hr. The remaining experiments (2, 3 and 6) were not conducted since the earlier ones indicated

TABLE 1  
LATIN SQUARE PLAN

Variables

Ammonia Concentration( %)			Nitrocellulose Concentration( %)			Reaction Time (hr)		
a <sub>1</sub>	-	5	b <sub>1</sub>	-	5	c <sub>1</sub>	-	4
a <sub>2</sub>	-	10	b <sub>2</sub>	-	10	c <sub>2</sub>	-	7
a <sub>3</sub>	-	15	b <sub>3</sub>	-	15	c <sub>3</sub>	-	12

Matrix

	b <sub>1</sub>	b <sub>2</sub>	b <sub>3</sub>
a <sub>1</sub>	c <sub>1</sub>	c <sub>2</sub>	c <sub>3</sub>
a <sub>2</sub>	c <sub>2</sub>	c <sub>3</sub>	c <sub>1</sub>
a <sub>3</sub>	c <sub>3</sub>	c <sub>1</sub>	c <sub>2</sub>

Suggested Experiments

- |   |   |   |
|---|---|---|
| 1. a <sub>1</sub> b <sub>1</sub> c <sub>1</sub> | 4. a <sub>2</sub> b <sub>1</sub> c <sub>2</sub> | 7. a <sub>3</sub> b <sub>1</sub> c <sub>3</sub> |
| 2. a <sub>1</sub> b <sub>2</sub> c <sub>2</sub> | 5. a <sub>2</sub> b <sub>2</sub> c <sub>3</sub> | 8. a <sub>3</sub> b <sub>2</sub> c <sub>1</sub> |
| 3. a <sub>1</sub> b <sub>3</sub> c <sub>3</sub> | 6. a <sub>2</sub> b <sub>3</sub> c <sub>1</sub> | 9. a <sub>3</sub> b <sub>3</sub> c <sub>2</sub> |

TABLE 2  
ADDITIONAL EXPERIMENTS

- |  |   |  |
|--|---|--|
| 10. a <sub>2</sub> b <sub>1</sub> c <sub>1</sub> | 12. a <sub>1</sub> b <sub>2</sub> c <sub>3</sub>              | 14. a <sub>2</sub> b <sub>2</sub> c <sup>x</sup> |
| 11. a <sub>3</sub> b <sub>1</sub> c <sub>1</sub> | 13. a <sub>2</sub> b <sub>2</sub> c <sub>2</sub> <sup>w</sup> | 15. a <sub>2</sub> b <sup>y</sup> c <sup>z</sup> |

w - 8 hr. instead of 7 hr., x - 10 hr. instead of 7 hr.

y - 20% instead of 15%, z - 24 hr.

time to be a governing factor. Additional experiments, 10-15 (see Table 2) were completed to provide needed data. In experiment number 12, the concentration of ammonia was reduced from 10% to 5%, resulting in 4% unreacted nitrocellulose. In experiment number 13, the percentage of ammonia was increased to 10% and the reaction time was reduced from 12 to 8 hr.; again, incomplete reaction resulted (1.6% unreacted nitrocellulose). However, a reaction time of 10 hr., keeping the other reaction conditions the same, did give complete decomposition (see experiment number 14). The completed reaction within this time frame required a 5.2:1 ratio of molar equivalents of ammonia to nitrocellulose. In order to determine the excess ammonia, experiment number 14 had to be repeated and the ammonia not used in the reaction was determined to be 48% of the original amount.

Since 48% ammonia remained, a final experiment was carried out in which the ammonia content (10%) was more efficiently used to decompose a larger amount of nitrocellulose (20%). This factor of course necessitates a longer reaction time. The ratio of molar equivalents of ammonia to nitrocellulose in this reaction was 2.6:1. After 24 hr., analysis of both the residual solids and the filtrate showed that no nitrocellulose remained. Titration of the residual ammonium hydroxide showed that 15% of the original amount of ammonia used remained in excess.

### EXPERIMENTAL

General. Infrared spectra were recorded with a Perkin-Elmer Model 27 Spectrophotometer using NaCl matched cells. A Corning Model 119 pH meter was used for pH determinations. Solutions were

concentrated under diminished pressure below  $60^{\circ}\text{C}$  using a Buchi Rotavapor R. Polaroid photomicrographs were taken using the optical microscope, a Polaroid Land camera and magnification of 2K was accomplished using a Coates and Water Electron microscope at 17 KV. The nitrocellulose used was supplied as a 30% aqueous slurry by Radford Army Ammunition Plant, Radford, Virginia. It was dried by heating in a vacuum oven at  $50^{\circ}\text{C}$  under diminished pressure to a constant weight.

#### Solubility of Nitrocellulose in Water

Experiments were carried out in which a specific weight of nitrocellulose (0.228 to 0.505 g)/was stirred for 24 hr. at room temperature in 950 ml. of distilled water. The insoluble nitrocellulose was recovered by filtration using a 0.22  $\mu\text{m}$  solvinert Millipore filter and dried in the vacuum oven. The range of p.p.m. of nitrocellulose not retained on the filter was 0-3.5 p.p.m. The filtrate was concentrated to dryness and the range of p.p.m. recovered was 0-3.

#### Quantitative Analysis for Nitrocellulose Using Infrared Spectroscopy

Since nitrocellulose is practically insoluble in water as shown by the previous solubility experiments, all aqueous samples were filtered through a 0.22  $\mu\text{m}$  solvinert Millipore filter. This pore size was chosen because it ensured complete removal of all micro-particles. The solid residue was dissolved in a known volume of acetone and the absorbance measured at the  $825\text{ cm}^{-1}$  frequency range. For low, medium and high concentrations of nitrocellulose, the 0.5, 0.103 and 0.04 mm. sodium chloride cells were used respectively. The concentration of nitrocellulose was then read from a straight line

calibration curve which was obtained by plotting absorbance readings vs. concentration of standard nitrocellulose solutions (see Figure 3). In cases where considerable amounts of inorganic nitrate could be present, the absorbance measurements were taken at the  $1650\text{ cm}^{-1}$  frequency range using tetrahydrofuran as solvent. The concentration of nitrocellulose was obtained from a previously prepared calibration curve.

#### Use of Sodium Hydroxide to Decompose Nitrocellulose

a. Dried nitrocellulose (5.0 g.) in 2% aqueous sodium hydroxide (100 ml.) was stirred and heated at  $95^{\circ}\text{C}$  for 30 minutes. The darkly colored reaction mixture was cooled and neutralized to pH 6.5 using 50% acetic acid before filtration. Filtration through a Millipore solvinert filter ( $0.22\text{ }\mu\text{m}$ ) gave 1.54 g (31%) of residual solids which were shown to be unreacted nitrocellulose by the infrared procedure.

b. Dried nitrocellulose (5.0 g.) in 3% aqueous sodium hydroxide (100 ml.) was stirred and heated at  $95^{\circ}\text{C}$  for 30 minutes. Using the above procedure it was found that 0.27 g. (5%) of unreacted nitrocellulose remained.

c. Dried nitrocellulose (5.0 g.) in 3% aqueous sodium hydroxide (100 ml.) was stirred and heated at  $98^{\circ}\text{C}$  for 30 minutes. Using the above procedure, it was found that 0.16 g. (3%) of unreacted nitrocellulose remained. The filtrate was concentrated to dryness and examined using the infrared procedure. No nitrocellulose was found in the filtrate.

d. Dried nitrocellulose (5.0 g.) in 3% aqueous sodium hydroxide (100 ml.) was heated at  $98^{\circ}\text{C}$  for 1 hr. Infrared spectroscopic quantitative analysis showed no nitrocellulose remained.

### Preliminary Attempts to Decompose Nitrocellulose Using Ammonium Hydroxide

a. Dried nitrocellulose (0.25 g.) in 10% ammonium hydroxide (50 ml.) was left for 16 hr. at room temperature. Visual and microscopical examination showed practically no decomposition of nitrocellulose.

b. Dried nitrocellulose (2.5 g.) in 29% ammonium hydroxide (50 ml.) was left 120 hr. at room temperature with intermittent stirring. Following the same procedure as that used for the sodium hydroxide treatment, it was found that 0.99 g. (40%) residual solids were collected. Of this, the infrared spectroscopic procedure showed that 0.08 g. (3%) unreacted nitrocellulose remained.

c. Dried nitrocellulose (2.5 g.) in 10% ammonium hydroxide (50 ml.) was heated at 40°C for 104 hr. Using the above procedure it was found that 0.17 g. (7%) unreacted nitrocellulose remained.

d. Dried nitrocellulose (2.5 g.) in 10% ammonium hydroxide (50 ml.) was stirred and heated at 98°C for 50 min. Visual and microscopical examination indicated about 50% decomposition.

### General Procedure for Degradation of Nitrocellulose Using Ammonium Hydroxide

A specific weight of dried nitrocellulose was placed in a 250 ml. round bottom flask fitted with a reflux condenser. The desired volume of a specific concentration of ammonia in water was added and the mixture stirred magnetically at a temperature of  $73 \pm 1^\circ \text{C}$  for the designated length of time. The reaction mixture was cooled to room temperature and filtered through a tared 0.22  $\mu\text{m}$  solvinert millipore filter. The residual solids were washed using hot distilled water until the filtrate was colorless. The residual solids were dried to a constant weight in a vacuum oven at 50°C and examined using the infrared



absorption procedure. For experiments in which the nitrocellulose content of the residual solids was zero, the filtrate was concentrated and the resulting residue examined for the presence of nitrocellulose. Commercially available ammonium hydroxide reagent (28-30% ammonia in water) was diluted with distilled water to obtain the desired concentration.

#### Effect of Time on Decomposition of Nitrocellulose

Using the above general procedure, nitrocellulose (5.0 g.) in 10% ammonium hydroxide (100 ml.) was heated for periods 4, 8, 16 and 23 hr. The results are listed below:

<u>Reaction Time (hr.)</u>	<u>Recovered Solids (%)</u>	<u>Unreacted Nitro- cellulose (%)</u>
4	10	Positive
8	3.2	0
16	1.5	0
23	1.0	0

#### Latin Square Design for Experiments

A Latin Square plan was used as an aid in optimizing the reaction conditions, the three variables being concentration of ammonium hydroxide (a), concentration of nitrocellulose (b) and time (c). The concentrations of ammonium hydroxide chosen were 5% ( $a_1$ ), 10% ( $a_2$ ) and 15% ( $a_3$ ). The concentration of nitrocellulose chosen were 5% ( $b_1$ ), 10% ( $b_2$ ) and 15% ( $b_3$ ). The length of reaction times chosen were 4 hr. ( $c_1$ ), 7 hr. ( $c_2$ ) and 12 hr. ( $c_3$ ). The experiments were performed according to the general procedure and the results are listed in Table 3.

TABLE 3

Results of Latin Square Experiments

Experiment No.	Latin Square Designation	Molar Equiv. of $\text{NH}_3$ to Nitrocellulose	Recovered Solids (%)	Unreacted Nitrocellulose
1	$a_1b_1c_1$	5.2:1	58	39
2	$a_1b_2c_2$	2.6:1		
3	$a_1b_3c_3$	1.7:1		
4	$a_2b_1c_2^w$	10.4:1	3	0
5	$a_2b_2c_3$	5.2:1	1.7	0
6	$a_2b_3c_1$	3.5:1		
7	$a_3b_1c_3$	15.6:1	0.9	0
8	$a_3b_3c_2$	5.2:1	4.9	0.8
9	$a_3b_2c_1$	7.8:1	12	5

Results of Additional Experiments

10	$a_2b_1c_1$	10.4:1	9.9	Yes*
11	$a_3b_1c_1$	15.6:1	6.5	Yes*
12	$a_1b_2c_3$	2.6:1	12.9	4
13	$a_2b_2c_2^w$	5.2:1	5.8	1.6
14	$a_2b_2c^x$	5.2:1	3.3	0
15	$a_2b^y c^z$	2.6:1	3.4	0

w - 8 hr. instead of 7 hr., x - 10 hr. instead of 7 hr., y - 20 % instead of 15%,  
z - 24 hr. \* - not determined quantitatively.

Experiment Nos. 2, 3 and 6 were not attempted.

### Determination of Excess Ammonia After Using 10% Ammonium Hydroxide to Decompose Nitrocellulose

Experiment number 14 listed in Table 3 was repeated. Dried nitrocellulose (5.0 g.) was treated with 10% ammonium hydroxide (50 ml.) for 10 hr. according to the general procedure. The mixture was cooled and the excess ammonia titrated using 117 ml. of 1.05 N nitric acid. It was determined that only 52% of the available ammonium hydroxide had been used in the reaction and therefore 48% remained in excess.

### A More Efficient Use of Ammonium Hydroxide per Gram of Nitrocellulose to Effect Complete Decomposition

Dried nitrocellulose (10.0 g.) was treated with 10% ammonium hydroxide (50 ml.) for 24 hr. according to the general procedure. These quantities represent a 2.6:1 molar ratio of ammonium hydroxide to nitrocellulose. Filtration gave 0.34 g. (3.4%) of recovered solids; however, analysis using the infrared spectroscopic procedure showed no nitrocellulose. The filtrate was concentrated and analyzed and again no nitrocellulose was found. This experiment was repeated and the excess ammonia titrated using nitric acid. It was determined that 15% of the original amount of ammonium hydroxide remained in excess.

### CONCLUSIONS

1. The infrared spectroscopic procedure can be used to quantitatively analyze for nitrocellulose in the presence of other cellulosic compounds and in the presence of inorganic nitrates. It is capable of measuring nitrocellulose down to the 1-5 p. p. m. range.

2. Using a strong base such as sodium hydroxide, a 3% aqueous solution of sodium hydroxide can decompose 97% of a 5% dispersion of nitrocellulose at  $98^{\circ}\text{C}$  in 30 min., in one hour the nitrocellulose has been completely decomposed.

3. Using a weak base such as ammonia in water, two sets of reaction conditions have been shown to be operative in causing complete decomposition. The choice is dependent on economic considerations.

a. If shorter reaction times are desired, a 10% dispersion of nitrocellulose can be decomposed completely in 10 hrs. at  $73^{\circ}\text{C}$  using a 10% solution of ammonia in water.

b. If economics dictates a more efficient use of the ammonia in water concentration, necessitating longer reaction times, a 20% dispersion of nitrocellulose can be decomposed completely in 24 hrs. at  $73^{\circ}\text{C}$  using a 10% solution of ammonia in water.

## BIBLIOGRAPHY

1. H. Muraour, Bull. soc. chim., 3, 265-7(1936).
2. E. Knecht and B. R. Bostock, J. Soc. Chem. Ind., 39, 163T (1920).
3. R. C. Farmer, J. Chem. Soc., 117, 806 (1920).
4. T. Urbanski, Chem. and Technology of Explosives, Vol. 2, p. 304.
5. A. Béchamp, Compt. rend., 41, 817 (1855).
6. H. Vohl, Dinglers Polytech. J., 112, 236 (1849).
7. E. Berl and A. Fodor, Z. ges. Schiess- u Sprengstoffw., 5, 296 (1910).
8. O. Silberrad and R. C. Farmer, J. Chem. Soc., 89, 1759 (1906).
9. T. M. Lowry, K. C. Browning and J. W. Farmery, J. Chem. Soc., 117, 552 (1920).
10. E. M. Berl and W. Smith, Jr., J. Soc. Chem. Ind., 27, 534 (1908).
11. W. O. Kenyon and H. LeB. Gray, J. Amer. Chem. Soc., 58, 1422-7 (1936).
12. S. N. Danilov and L. I. Mirlas, J. Gen. Chem. (U.S.S.R.) 4, 817-29 (1934).
13. R. Chernitskaya, V. Kargin and D. Gutenmakher, J. Applied Chem. (U.S.S.R.) 13, 1159-64 (1940).
14. H. Ambrohn, J. Soc. Chem. Ind., 32, 991 (1913).
15. H. Molisch, Monatsch. Chem., 7, 108 (1886).
16. H. M. Rosenberger and C. J. Shoemaker, Anal. Chem., No. 8, 31, 1315 (1959).
17. H. Levitsky and G. Norwitz, Anal. Chem., No. 9, 34, 1167 (1962).
18. T. Wendt and A. Kaplan, in preparation.
19. G. Meiszner, Z. ges. Schiess-Sprengstoffw., 8, 252-4 (1912).